



STUDY ON OPTIMUM CONDITION IN pH SOLUTION  
OF RICE HUSK BASED SUPERABSORBENT POLYMER  
COMPOSITE.

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## **STUDY ON OPTIMUM CONDITION IN pH SOLUTION OF RICE HUSK BASED SUPERABSORBENT POLYMER COMPOSITE**

### **ABSTRACT**

Poly Rice Husk-Acrylic acid-co-Acrylamide superabsorbent polymer composite (RH-AA-AM SAPC) was synthesized by solution polymerization of the Acrylic Acid (AA) and Acrylamide (AM) monomer onto RH fibre using Ammonium Persulphate (APS) and N, N- methylene bisacrylamide (MBA) which act as an initiator and crosslinker, respectively. The optimal conditions for synthesizing the polymer with the highest water absorbency have been identified by studying the water absorption of the polymer with the effect of initiator, crosslinking agent and filler amounts. Maximum water absorbency of RH-AA-AM SAPC was achieved at 10 wt% on initiator, 0 wt% of crosslinking agent and 10 wt% of filler amount which results on 115.5155 g/g, 91.4020 g/g, and 44.7940 g/g water absorbency. Finally, the optimum water absorbency in pH solution was observed at pH 4 for all parameters varies. The samples were characterized by using Fourier Transform Infrared (FTIR) analysis, Thermogravimetric Analysis (TGA) and Field Emission Spectroscopy Electron Microscopy (FESEM). The TGA analysis shown that thermal stability of RH-AA-AM SAPC was better than Pure SAP, meanwhile FTIR analysis shown RH-SAPC have sharp peak of bonding curve shape to Pure SAP.

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### **ABSTRAK**

Poli Sekam Padi-Akrylik acid-co-Akrilamida komposit polimer penyerap lampau (RH-AA-AM SAPC) disintesis melalui polimerisasi larutan Asid Akrylik (AA) dan Akrilamida (AM) adalah monomer kepada serat RH menggunakan Amonium Persulfat (APS) dan N, N-metilen bisacrylamide (MBA) dengan masing-masing sebagai pemula dan pemaut silang. Kondisi optimal untuk sintesis polimer dengan serapan air tertinggi telah diperhatikan dengan kondisi yang berbeza seperti kesan dari segi kuantiti pemula, pemaut silang, dan kuantiti pengisi. Penyerapan air serap yang maksimum oleh RH-AA-AM SAPC dicapai pada 10% berat kuantiti pemula, 0% berat kuantiti pemaut silang dan 10% berat kuantiti pengisi masing-masing menghasilkan 115.5155 g / g, 91.4020 g / g dan 44.7940 g / g serapan air. Akhirnya, daya serap air yang tinggi dalam larutan pH diamati optimum pada pH 4 untuk semua parameter bervariasi. Struktur RH-AA-co-AM SAPC dianalisis dengan cara menggunakan alat Field Emission Scanning Electron Microscopy (FESEM) untuk mengidentifikasi struktur pori superabsorbent yang disintesis. Akhirnya serap air tinggi dalam larutan pH diamati pada optimum pada pH 4 untuk semua parameter bervariasi. Sampel dikarakterisasi dengan menggunakan Fourier Transform Infrared (FTIR) analisis, Analisis Termogravimetri (TGA) dan Field Emission Spectroscopy Electron Microscope (FESEM). Analisis TGA menunjukkan bahawa stabiliti termal RH-AA-AM SAPC lebih baik dari komposit polimer super serapan tulen (SAP), sementara analisis FTIR menunjukkan RH-SAPC menunjukkan memiliki bentuk melengkung yang tajam berbanding dengan bentuk melengkung SAP. .

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## LIST OF ABBREVIATIONS

RH	Rice Husk
SAPC	Superabsorbent Polymer Composites
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
SAP	Superabsorbent Polymer (synthetic)
SPAN	Starch-graft-polyacrylonitrile
AA	Acrylic Acid
APS	Ammonium persulphate
MBA	N,N'-methylenebisacrtlamide
AM	Acrylamide
HCl	Hydrochloric acid
NaOH	Sodium Hydroxide
NaCl	Sodium Chloride

N <sub>2</sub>	Nitrogen
CTAB	Cetyltrimethylammonium Bromide
CMCTS-g-PAA	Carboxymethylchitosan-g-poly (acrylic acid)
OPEFB	Oil Palm Empty Fruit Bunch
OPEFB-g-PAAm	Oil Palm Empty Fruit Bunch-graft-poly(acrylamide)
PAA	Poly(acrylic acid)
CMCTS	Carboxymethylchitosan
CMTCTS-g-(PAA-co-PDMAAC)	Carboxymethyl chitosan-g-poly(acrylic acid-co-dimethyldiallylammonium chloride)
PDMAAC	Dimethyldiallylammonium Chloride
PAA-AM/SH	Poly(acrylic acid-co-acrylamide)/ sodium humate
WS	Wheat-Straw

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 BACKGROUND OF STUDY**

Superabsorbent polymer (SAP) is a material that can absorb a large amount of fluids such as water compared with general absorbing materials and the absorbed water is hardly removable (Mohan et al., 2005). This phenomenon occurs because SAP has cross-linked networks of hydrophilic polymer chains which also known as a hydrogels that can absorb the fluids in a large amounts from their size and weight (Zohurriaan and Kabiri, 2008). SAP able to absorb large quantities of water, ranging from hundreds to thousands of times from their own weight even under some pressure applied. It has been extensively applied as sorbents in personal-care products, including infant diapers, feminine hygiene products, medical, pharmaceutical fields, textile industrial, agricultural industry and incontinence products (Yu and Hui-min, 2006).

The first introducing of SAP is when acrylic acid (AA) and divinylbenzene undergoes thermal polymerization in an aqueous medium in late 1983s. Then, SAP was developed into new generation of SAP which hydrogels in era 1950s. In year 1970s, the first commercial SAP was introduced by undergoes alkaline hydrolysis process of starch-graft-polyacrylonitrile (SPAN). Then, after 8 years of SPAN was introduced, Japan developed more SAP materials to be used in their feminine industry (Zohuriaan and Kabiri, 2008).

Results from the excellent properties relative to traditional water absorbing materials such as sponge, cotton and pulp, SAP are widely used in many fields such as in hygienic products, horticulture, gel actuators, drug-delivery system and coal watering (Zhang et al., 2007). SAP application on agriculture area was used as a varies function such as soil amendments to improve physical properties of soil, macro-porous medium, retaining materials and also can act as a controlled release system by uptake some nutrient elements from soil (Zohuriaan and Kabiri, 2008). Meanwhile, according to Mohan et al (2005), the pH and temperature sensitive hydrogels are being used for various applications including controlled drug delivery system and immobilized enzyme system.

Currently, utilization of an inorganic material has drawn much attention and has been found in preparation of superabsorbent polymer composites by introducing starch, cellulose and lignin, inorganic clays and chitosan into pure polymeric superabsorbent. The main purpose of the addition of these inorganic materials is to improve swelling property and to ensure biodegradability of corresponding

superabsorbent materials (Zhang et al., 2007). As example, chitosan which is from natural polymer exhibiting several favorable properties, including good biodegradability, biocompatibility, antibacterial property and low toxicity that will enhance water absorbency in superabsorbent polymer industries (Hui-min and Yu, 2006).

Besides that, phyllosilicate which is organic clays is also one of the appropriate materials for preparing SAPC in polymer field due to the relative low production cost, high water absorbency and their considerable range of applications (Wang and Li, 2005). There are many types of phyllosilicate which is kaolinite, montmorillonite, hectrite, saponite and synthetic mica. However, the most commonly used in research is layered silicate a nanocomposite which belongs to the same general family of 2:1 layered phyllosilicate (Kiatkamjornwong, 2007). Besides that, previous study on agriculture waste, which is wheat-straw-poly (acrylic acid) SAPC, showed the highest absorbency was obtained at 20% of wheat straw (WS). This observation signifies that the presence and amount of WS plays an important role in affecting the equilibrium water absorbency of composites (Liang et al., 2009).

However, the present research is conducted on utilization of crops residues which is Rice Husk (RH) that obtained from agriculture waste biomass. Rice Husk is cheap and economical material which easily available. Rice Husk also has same composition with phyllosilicate where it also can form polymer composite and absorb more than pure SAP absorbent. It is expected that cellulose and lignin that

contained in RH could improve the swelling properties of SAPC (Rhman et al., 1997).

## **1.2 PROBLEM STATEMENT**

Poor in degradability of synthetic SAP as well as low water absorbency in product are the significant problem in SAP industry. Currently, a large amount which is approximately 80 million tons of rice husks were produced annually and contributed to environmental problems. Therefore, this research is aimed to minimize the problem by using rice husk as natural filler in the fabrication of SAPC. As the natural fillers is render the SAPC to make more biodegradable, therefore by using rice husk in this research, the produced SAPC is expected to be more environmental friendly. It also expected to enhance the water absorbency due to the high silica contents in rice husk. Moreover, it can be found abundantly in this country and will get free at paddy field waste.

This research is designed to determine the optimum condition on the amount of initiator, crosslinker, monomer and pH value in water absorbency of rice husk based superabsorbent polymer composites. So that, this research is focused to increase the water absorbency and swelling properties through the introduction of rice husk (RH) with reducing the environmental problem and discover the new absorbent for SAPC.



### **1.3 RESEARCH OBJECTIVE**

The objective of this research is to study the optimum conditions and physiological properties in pH solution of rice husk based superabsorbent polymer composite by determine:

- i. Effect on amount of filler, (RH) towards water absorbency.
- ii. Effect on amount of initiator, (APS) towards water absorbency.
- iii. Effect on amount of crosslinking agent, (MBA) towards water absorbency.

### **1.4 RESEARCH SCOPE**

In preparation of Rice Husk Superabsorbent Polymer Composite through solution polymerization at 80°C, the initiator (APS), monomer (AA and AM), crosslinking agent (MBA) and rice husk were diluted in a five-neck flask set up. To achieve the objective, this research had varied the parameters to investigate the amount towards water absorbency which is pH solution. In preparation of buffer solution, types of acid and alkali used to prepare buffer solution are hydrochloric acid (HCl) and sodium hydroxide (NaOH). The tea bag method used testing the RH-SAP in pH solution. The sample RH-SAP was characterized by using Fourier Transform Infra-Red Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Field Emission Scanning Electron Microscopy (FESEM).

## **1.5 SIGNIFICANCE OF STUDY**

The demanding on the high water absorbency in SAPC industry had force the researcher to find new materials from agriculture waste such as rice husk to avoid the environmental problem, lower water trap in diapers industry and other applications. Besides that, rice husk is produced naturally and biodegradable into soil. It also could easily be found as a waste material at rice factories and give benefit to the environment.

## **CHAPTER 2**

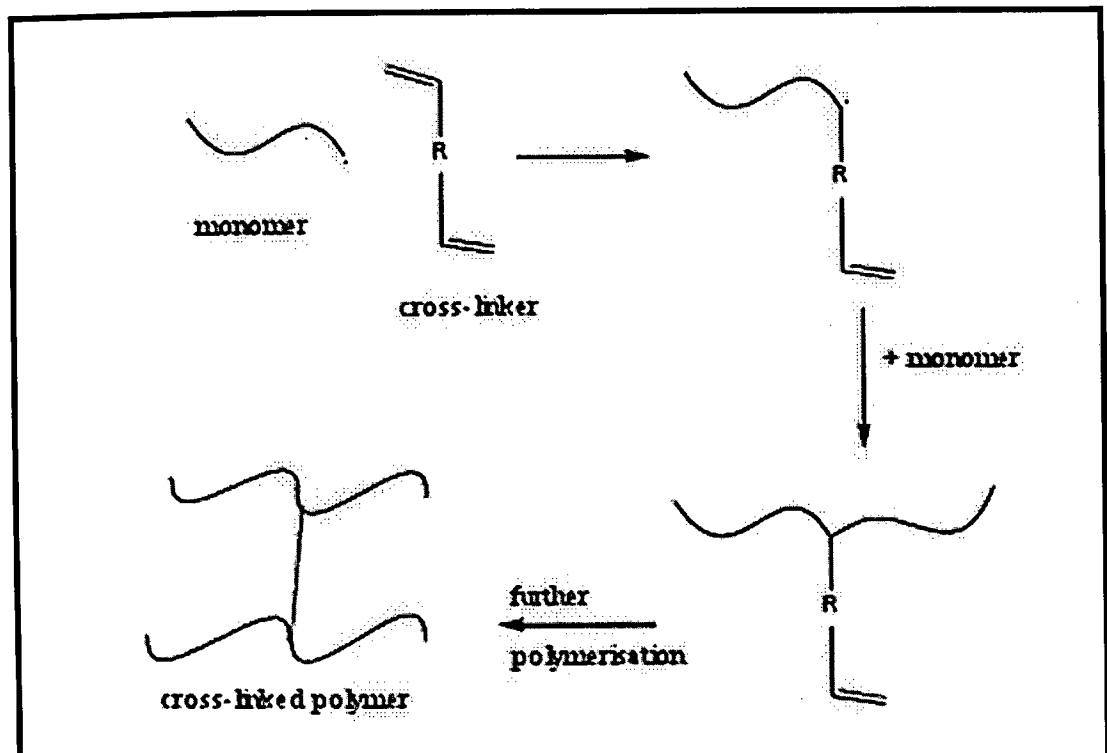
### **LITERATURE REVIEW**

#### **2.1 SUPERABSORBENT POLYMER COMPOSITES (SAPC)**

SAP was widely used in many areas as soon as discovered because of the excellent absorbent properties (Gualtieri, 2001). It can be considered that the absorbent property is one of the most important indicators of SAP materials which can be influenced by the interior factors of the materials and the external solutions (Long et al., 2011). According to Kiatkamjornwong, (2007) rubbery nature is one of the characteristic on swollen polymers which has been used to control the consistency of products as diverse cosmetics or concrete to contribute a soft, yet dry, feel to a product such hot or cold packs for sore muscles.

According to Zohurriaan and Kabiri, (2008) SAP can be classified into four groups based on the presence or absence of electrical charge located in the cross-linked chains which is non-ionic, ionic (including anionic and cationic), amphoteric electrolyte (ampholytic containing both acidic and basic groups and zwitterionic

Meanwhile, in solution polymerization co-polymerization/cross-linking reactions, the ionic or neutral monomers are mixed with the multifunctional cross-linking agent. The polymerization is initiated thermally by a redox initiator system. The presence of solvent serving as a heat sink is the major advantages of the solution polymerization over the bulk polymerization (Kiatkamjornwong, 2007).



**Figure 2.1:** The mechanism of reaction in solution polymerization

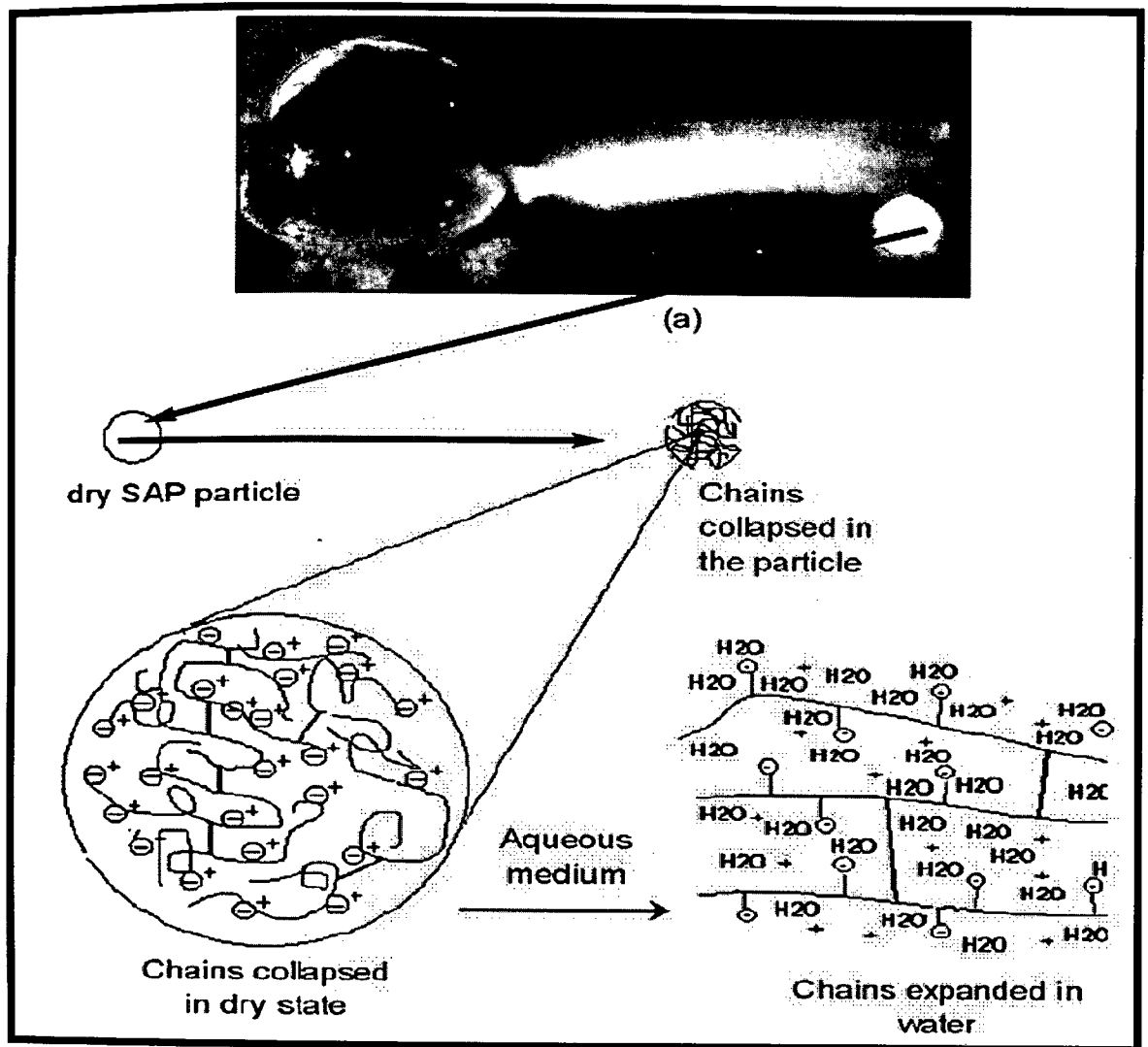
Source: Mark Elliott (2010)

According to Zohuriaan and Kabiri (2008), SAP could absorb fluids by two ways which is chemical absorption and physical absorption. In chemical absorption fluids were absorbed via chemical reaction meanwhile in physical absorption, fluids were absorbed via four mechanisms like:

- i) Reversible changes their crystalline structure such as silica gel and anhydrous inorganic salts
- ii) Physical entrapment of water through capillary force in their macro-porous structure such as soft polyurethane sponge
- iii) A combination between mechanism (ii) and hydration of functional groups such as tissue paper
- iv) And the last is combination between mechanism (ii) and (iii) and essentially dissolution and thermodynamically favoured expansion of the macro-molecular chains limited by cross-linkages.

All mechanism that mentioned above, explained how SAP can absorb and increase their size and weight.

Figure 2.2 shows structures of a dry SAP particle and in an aqueous medium. Based on the Figure 2.2, the chains were expanded in water and furthermore retain a large amount of water between the structures. In addition, water can retain because of the existence of hydrogen bonding in between the structure and water. As shown in Figure 2.2, the bonding can trap a lot of water between positive and negative charge.



**Figure 2.2:** Illustration of an acrylic-based anionic superabsorbent hydrogel: (a) The SAP single particle in dry (right) and water-swollen states (left). The sample is a bead prepared from the inverse-suspension polymerization technique. (b) A schematic presentation of the SAP swelling.

Source: Zohuriaan and Kabiri (2008).

Generally, the mechanism of water absorption of traditional and superabsorbents polymer is different. Traditional absorbent materials such as tissue papers and polyurethane foams usually will lose most of their absorbent water when they are squeezed. As comparison to traditional absorbents material, SAPC material will not lost their absorbent characteristic even it had been swollen in a long period in water or aqueous solution. This absorbent characteristics is due to the particle shape of SAP that present in a form of granule, fibre, film and others that be preserved after water absorption and swelling which prevent a loosening, mushy or slimy state (Zohuriaan and Kabiri, 2008).

Chitosan is another important natural polymer and have been modified via chemical reaction like reaction between with vinyl monomers and APS to produced superabsorbent polymer called carboxymethylchitosan (CMCTS-g-PAA). Hence, this SAPC shown that the rate of water absorbency of the polymer composites was high (Yu and Hui-min, 2006). This shows that by adding filler to SAPC system it will gives high water absorbency for this research.

The synthetic superabsorbent polymers like acrylamide (AM) was absorbed large amounts in fluid absorbing capacity but this synthetic polymers are poor in degradability especially for applications in agriculture and horticulture (Shafinaz and Shahrir,2011). Thus, in this research has been used AM and RH collaboration to produced superabsorbent polymer composite which will give degradable product and expected to have large amounts fluid absorbency capacity.

## 2.2 RICE HUSK (RH)

Rice husk is widely produced from waste of agriculture field which can be found abundantly in Malaysia. According to Oliver (2004), 20% of the paddy weight is husk and in the year of 2008, it has been reported that the world paddy production was approximately 661 million tons which contributes to 132 million tons of rice husk were produced. According to Oliver (2004), the rice husk is produced in the first step in the milling process when the husk is removed from the grain in the husking stage of the rice mill. Even though there are some uses for rice husk such as an improvement of quality concrete and renewable fuels due to it has high calorific value, it is still often considered as a waste product in the rice mill and often been burned dumped on wasteland.

Rice husk was chosen as a fiber in local uses because the granular structure, chemical stability and its local availability at very low cost and there is no need to regenerate them due to their low production cost. According to Nair and Sawant (2007), rice husk generally a cellulose 35%, hemicelluloses 25%, lignin 20%, and ash 17% by weight. However, Armesto et al., (2002) and Daifullah et al., (2003) states that the main constituents of rice husk are 64-74% volatile matter and 12-16% fixed carbon and 15-20% ash. Another claim is the rice husk compositions are 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, 1.82% extractives, 8.11% water and 15.05% mineral ash (Govindarao, 1980; Rhman et al., 1997; Nakbanpote et al., 2000).